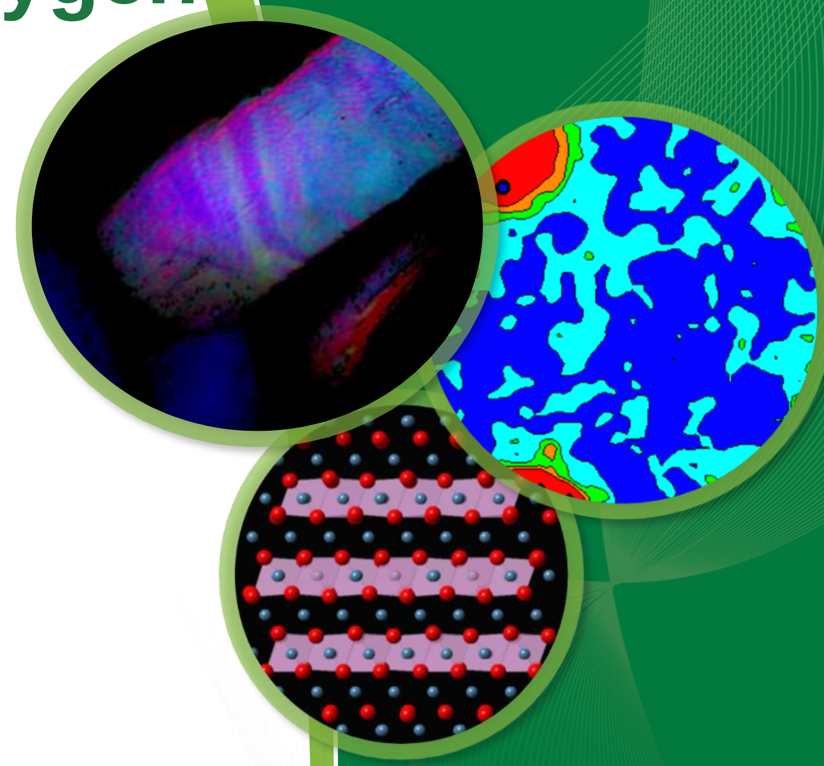
High Capacity Multi-Lithium Oxide Cathodes and Oxygen Stability



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Oak Ridge National Laboratory

2018 U.S. DOE Vehicle Technologies Office Annual Merit Review

June 19, 2018 **Project ID: BAT106**

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Overview

Timeline

- Project start date: Oct. 1, 2015
- Project end date: Sept. 30, 2018
- Percent complete: 100%

Barriers

Performance: High energy density for PEV applications with cell level targets ≥ 400 Wh/kg and 750 Wh/L
Life: 2000 deep discharges (SoC range) over the entire life
Safety: Thermally stable and abuse tolerant

Budget

- FY17 Funding: $ 400K
- FY18 Funding: $ 400K

Partners/Collaborators

- *Pacific Northwest National Laboratory*
  Electron Microscopy
- *Brookhaven National Laboratory*
  Synchrotron X-ray diffraction
- Lawrence Berkeley National Laboratory
  Modelling and insitu DEMS

OAK RIDGE National Laboratory

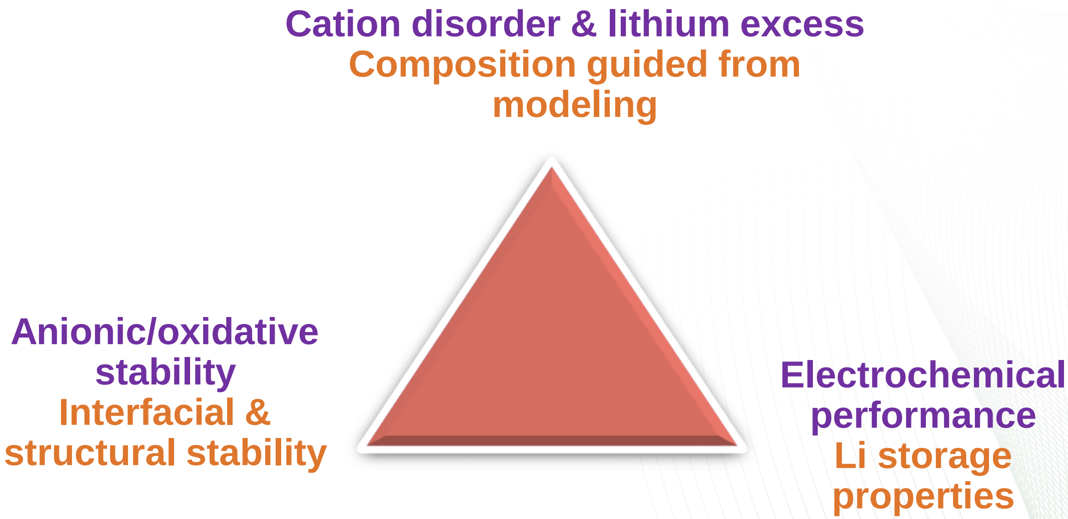
Relevance

Objectives :

(I) Develop high-voltage and high-capacity cathode materials for lithium-ion batteries to achieve Battery 500 goal of 500 Wh/kg for 1000 cycles.

(II) Recent studies have shown specific rock salt disorder lithium excess oxides enable high voltage stability with either minimal oxygen loss or reversible oxygen redox with no irreversible structural transformation.

(III) Most of the disordered oxides studied in this project belong to early transition metal (TM) group such as Mo, Cr, Ti with no cobalt.



Utilize cation-disorder as a means to optimize and stabilize high voltage cathodes

Milestones

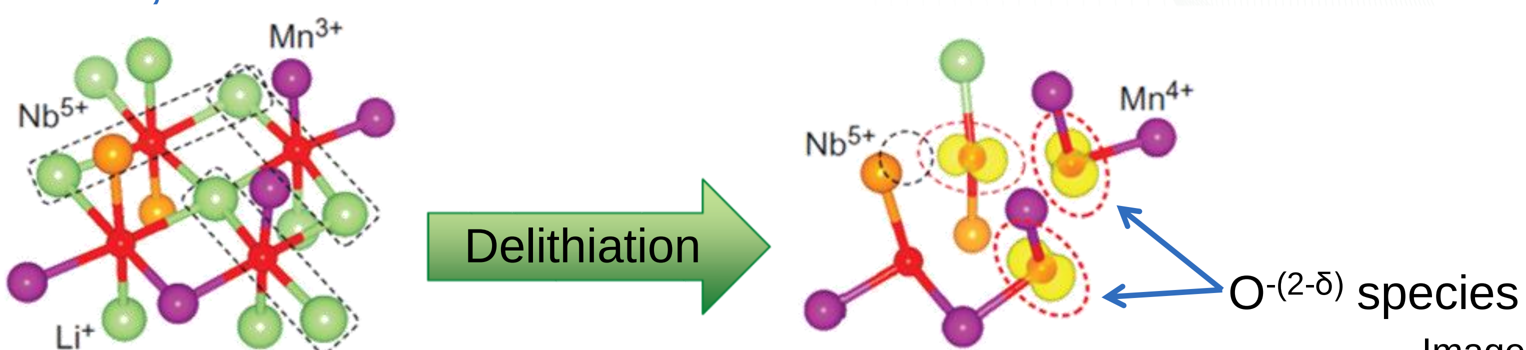
Due Date	Description	Status
06/30/2017 (Q3)	Synthesize one particular class and composition of cation disordered cathodes: Li_2MoO_3 and Cr - substituted Li_2MoO_3	Complete
09/30/2017 (Q4)	Complete structural and electrochemical performance analysis of disordered cathodes - Li_2MoO_3 and Cr substituted Li_2MoO_3 (No-Go) Revised to include Cr doped NMC and MoO_3 coated NMC	Complete
12/31/2017 (Q1)	Complete neutron powder diffraction, microstructural analysis and gas evolution studies of Li_2MoO_3 cathodes synthesized using solid state/sol-gel method as well as sputtered thin film electrodes with no binders and carbon. Evaluate and analyze oxygen stability between 4.3-4.8 V	Complete
03/31/2018 (Q2)	Synthesis and electrochemical performance testing of at least two composition of Mo doped Ni-rich NMC composition. Initially Mo doping will be varied between 3-10 %	Complete
06/30/2018 (Q3)	Synthesize one particular class and composition of disorder composite cathodes with Li_2MoO_3 as a structural unit for stabilizing the NMC cathodes. Continue looking for stable phases with the compositional space xLi_2MoO_3. (1-x) $LiMO_2$; with x = 0.2 - 0.4 and M = Mn, Ni, Co.	In progress
09/30/2018 (Q4)	Undertake structural and electrochemical performance analysis of disorder cathodes of few selected composition of xLi_2MoO_3. (1-x) $LiMO_2$ in order to get a mechanistic understanding of the oxygen stability and the role of disorder	In progress

Approach/Strategy

Design and synthesis of high-voltage, high-capacity lithium excess oxide cathodes guided by *state-of-the-art* characterization and modeling based on the following approach

- Mitigate and address unfavorable irreversible structural transition and oxygen loss in lithium excess TM oxides by effective control of cation mixing (disorder) during delithiation.
- In this specific approach substituting early transition metals such as Mo, Cr, and Ti in lithium excess rock salt cathode structures can provide high capacity and oxidative stability.
- **Oxygen participation in redox process**: Oxygen participation, commonly referred to as “anionic redox” could be a viable approach for obtaining high reversible capacity as reported in $Li_2Ru_{0.50}Sn_{0.50}O_3$ and $Li_{1.25}Mn_{0.50}Nb_{0.25}O_2$.
- Use in-situ and ex-situ local probe spectroscopy and microscopy to understand coupling between oxygen redox and cation disorder (migration)

Disordered, Li-excess Cathode



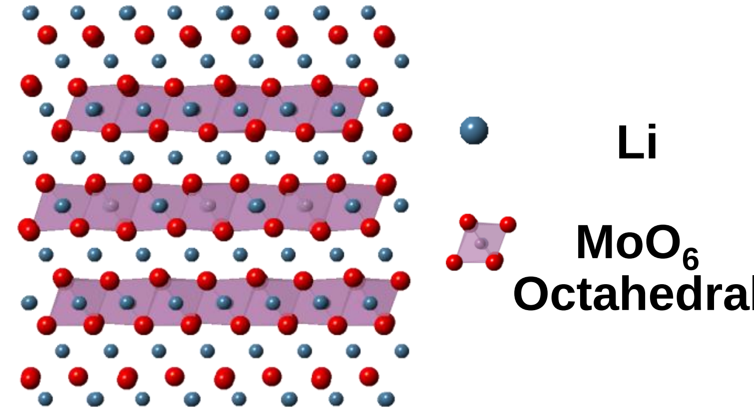
$Li_{1.25}Mn_{0.5}Nb_{0.25}O_2$ $Li_{0.25}Mn_{0.5}Nb_{0.25}O_2$

Images adapted with permission from: Seo et al. *Nat. Chem*, 2016, 8, 692.

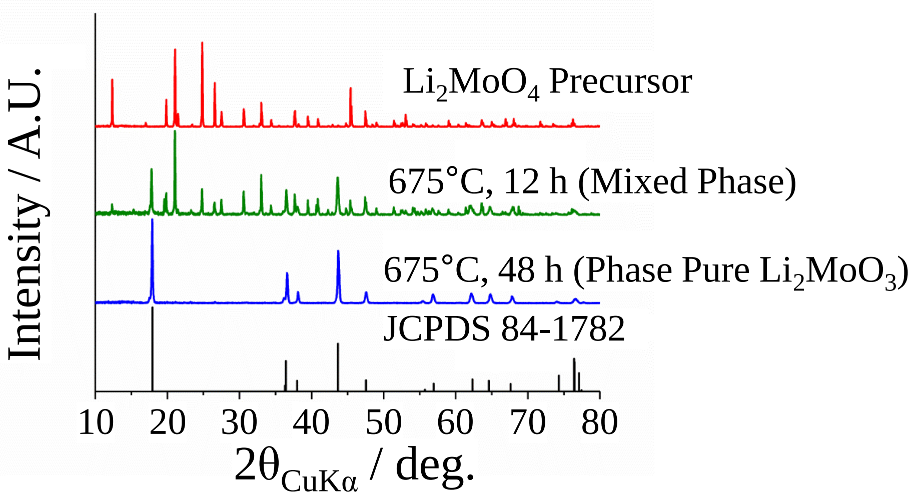
Li_2MoO_3 was synthesized and characterized as a structural unit that can be integrated to stabilize high voltage cathodes

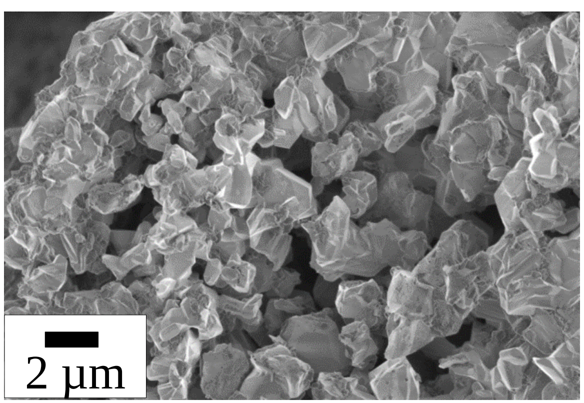
Li_2MoO_3 Synthesis Procedure

Precursor: Li_2MoO_4 powder (commercial)
Heating: Heat at 675 °C under flowing Ar/H_2 (96/4)

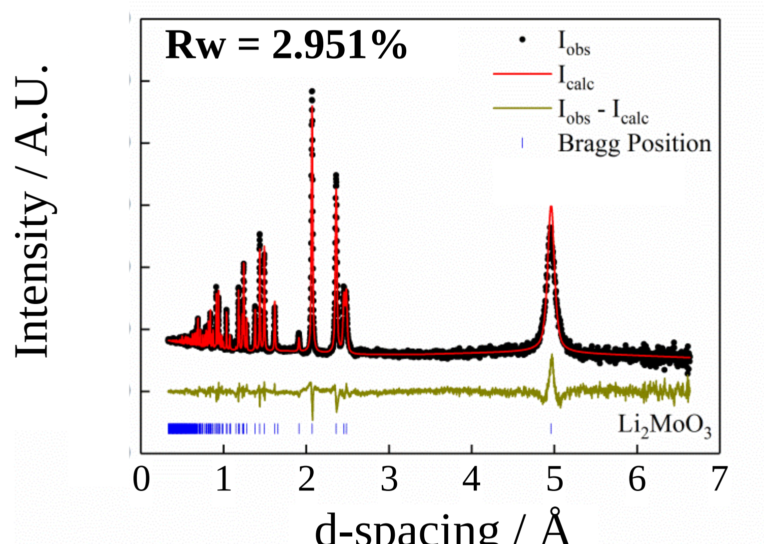


XRD (λ = 1.54 Å)





Neutron Diffraction (λ = 0.7Å)



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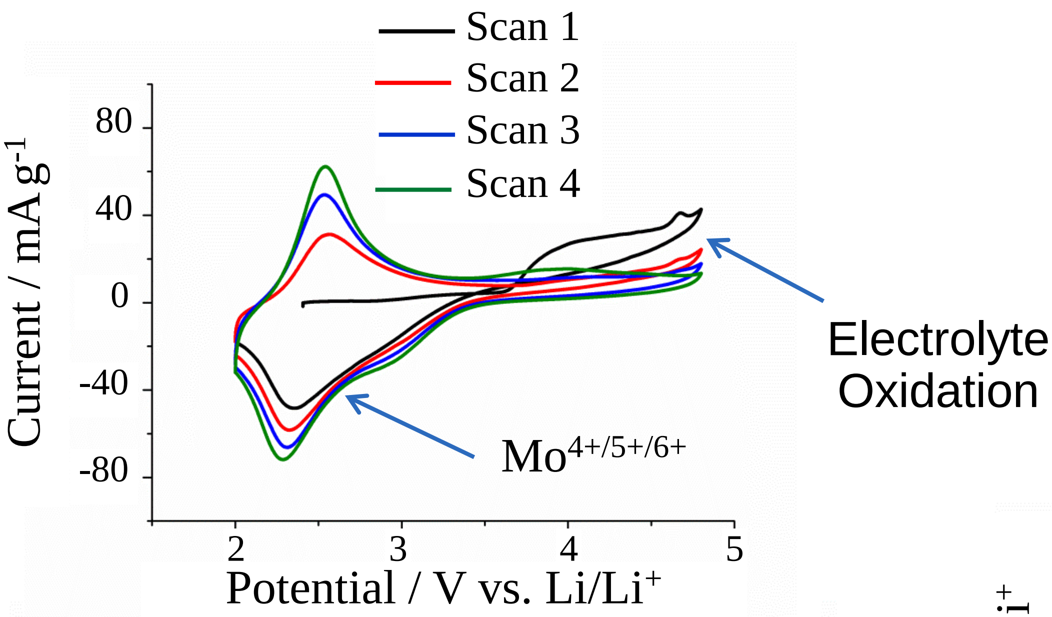
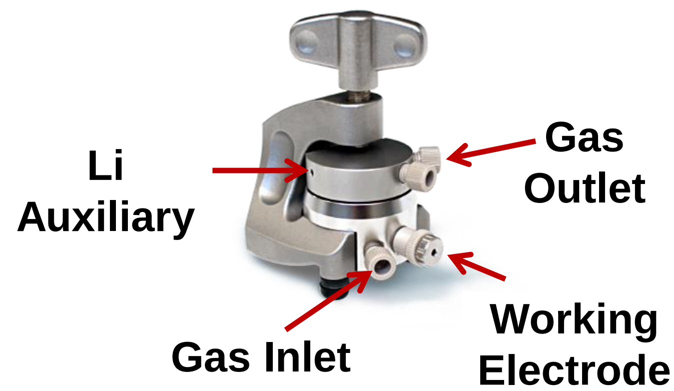
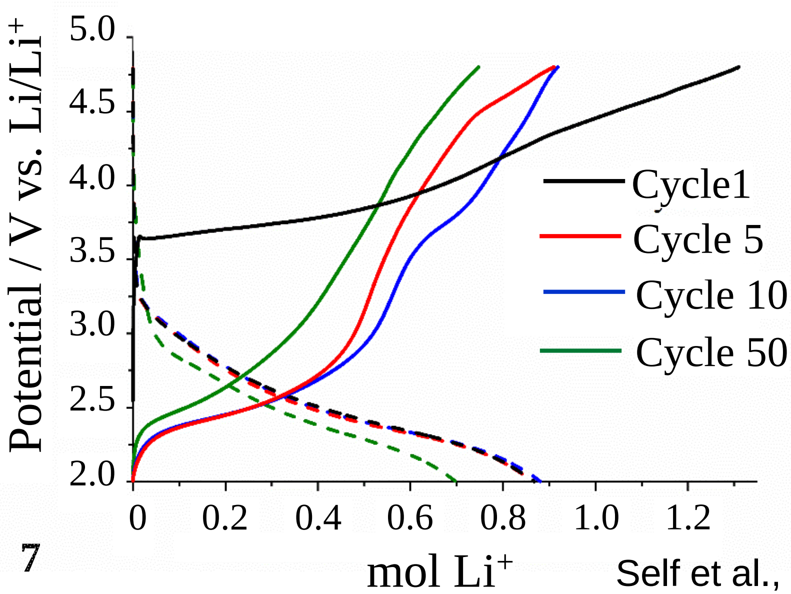
With Ashfia Huq, ORNL

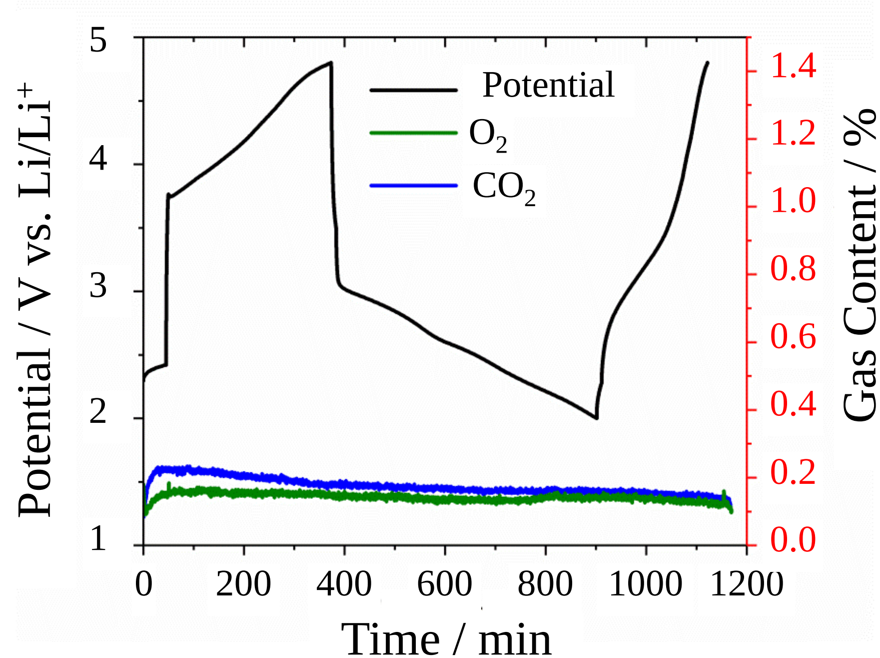
(I) Li_2MoO_3 electrodes are electrochemically active demonstrating up to 1 Li reversible capacity and (II) No significant oxygen evolution up to 4.8 V



In-Situ Mass Spectrometry







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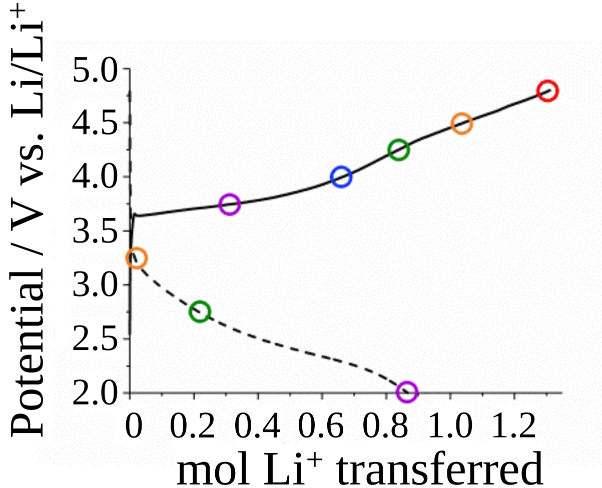
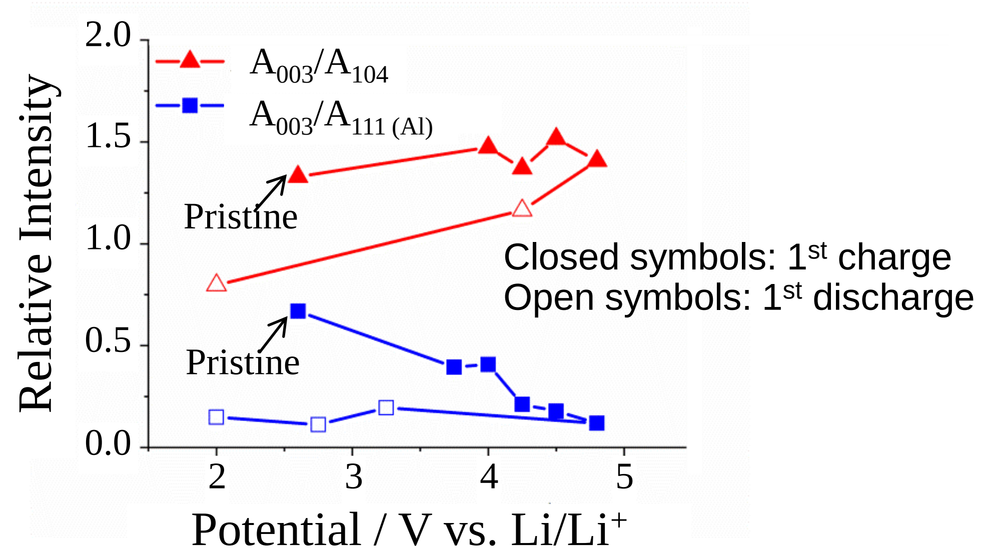
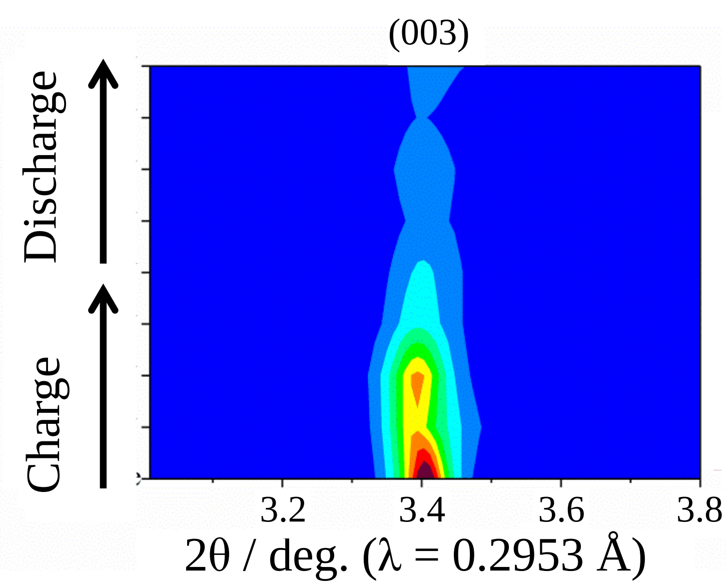
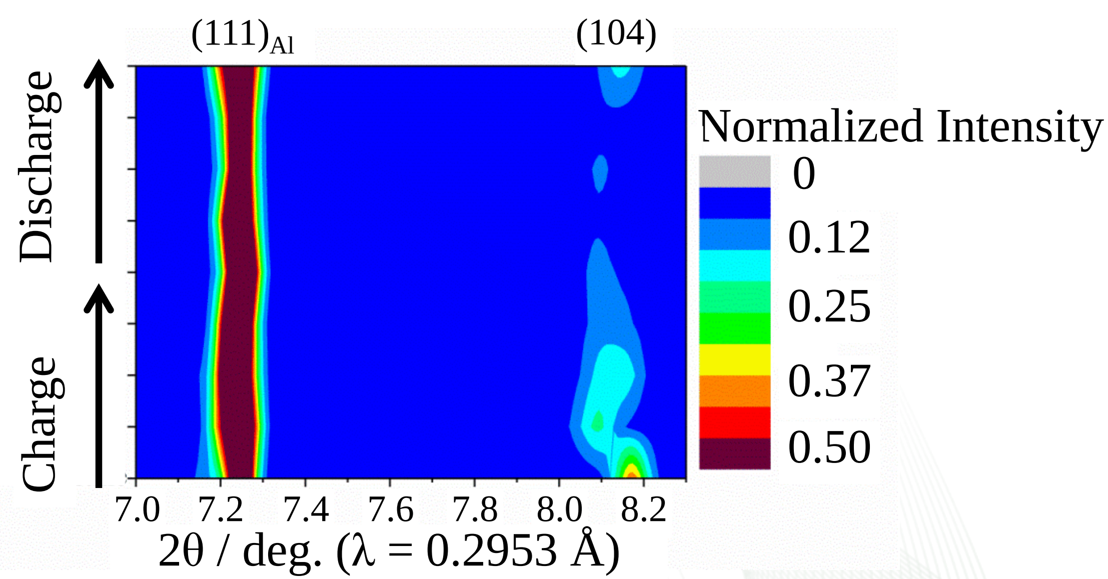
With G. Veith ORNL

Synchrotron XRD at different voltage (SoC) shows gradual loss of crystallinity for $Li_{2-x}MoO_3$







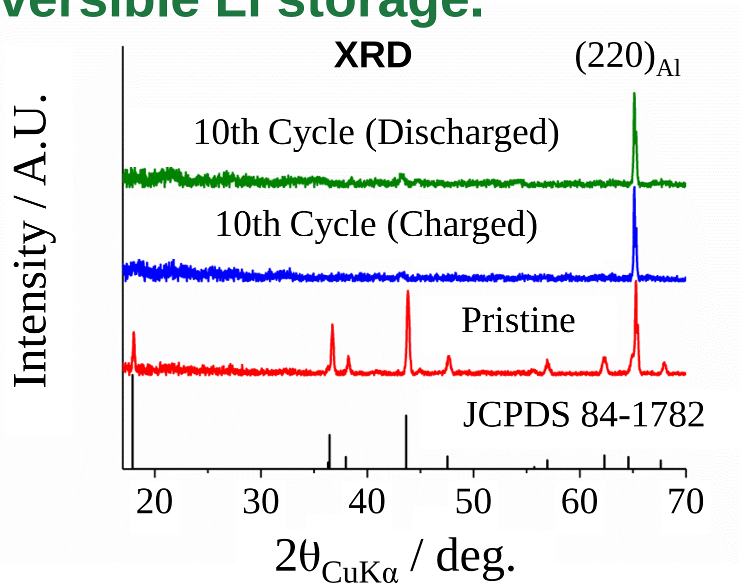


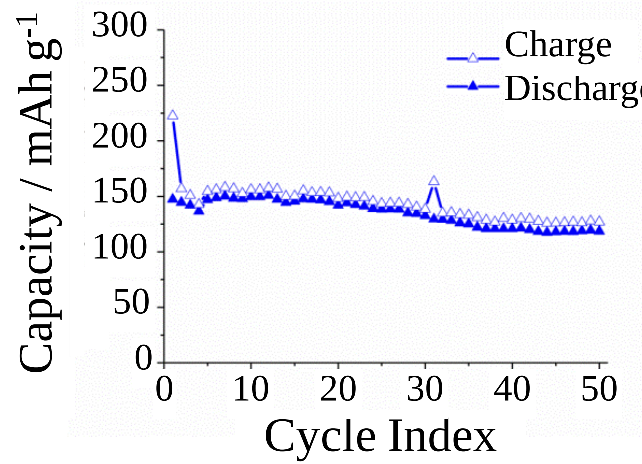
Collaboration with Feng Wang, Brookhaven National Laboratory

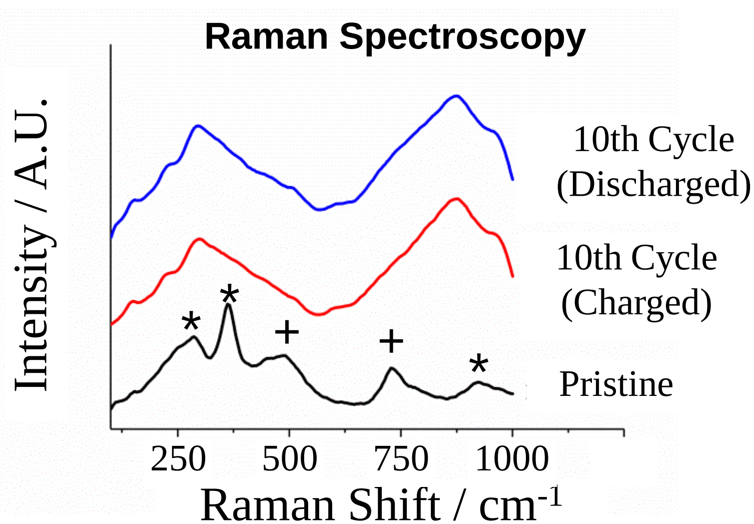
$Li_{2-x}MoO_3$ becomes less crystalline during first cycle

Technical Accomplishment

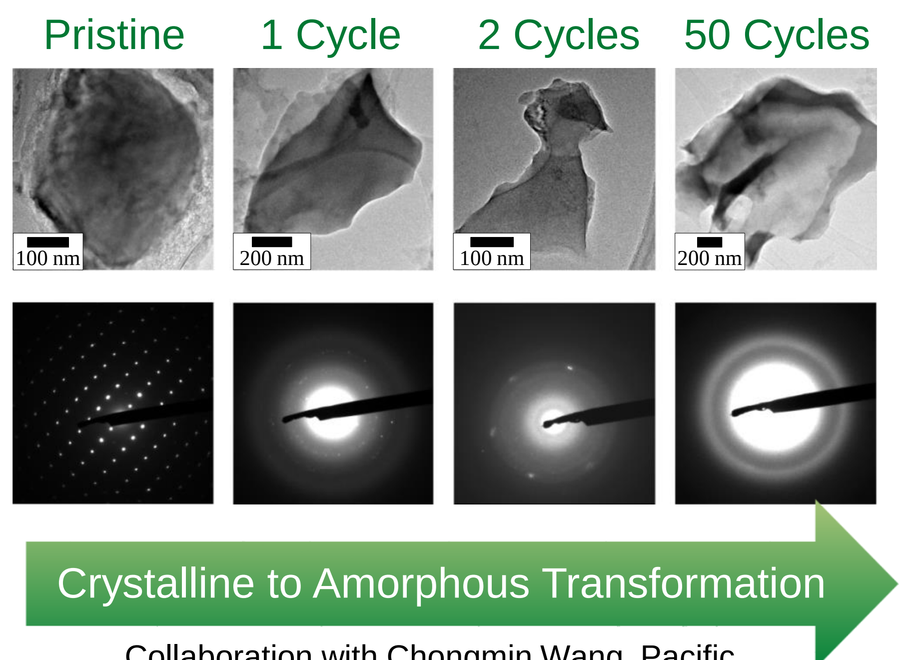
Combination of techniques show Li_2MoO_3 becomes mostly amorphous after several cycles. Interestingly, this amorphization does not prevent reversible Li storage.







* Mo=O vibrational modes
\+ Mo-O-Mo stretches



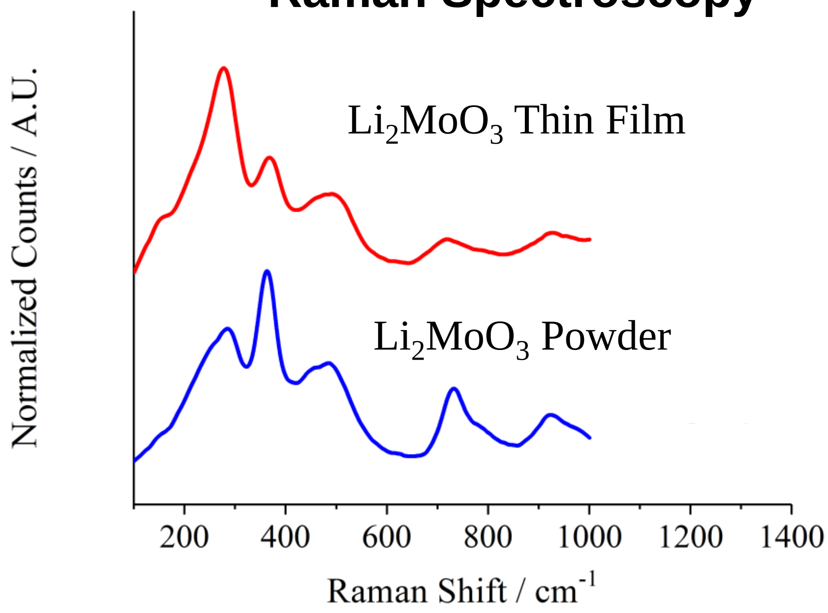
Collaboration with Chongmin Wang, Pacific Northwest National Laboratory

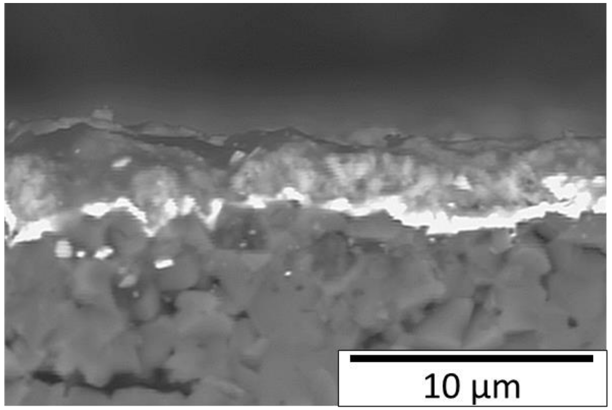
Thin film Li_2MoO_3 cathodes with no binder and carbon black were fabricated using R-F sputtering method for studying the structural changes and the electrode/electrolyte interface

Li_2MoO_3 sputtering conditions:

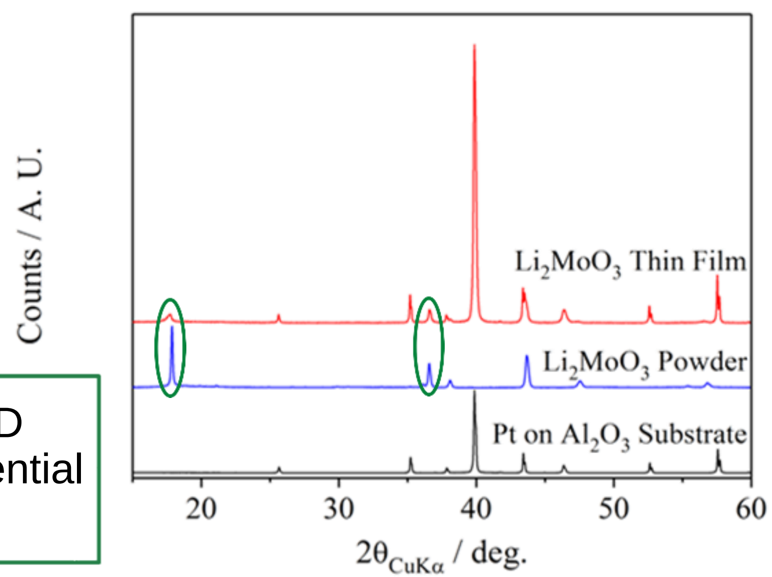
60 W, 20 mTorr Ar, 4.9 nm/min (1.01 mm)

Raman Spectroscopy





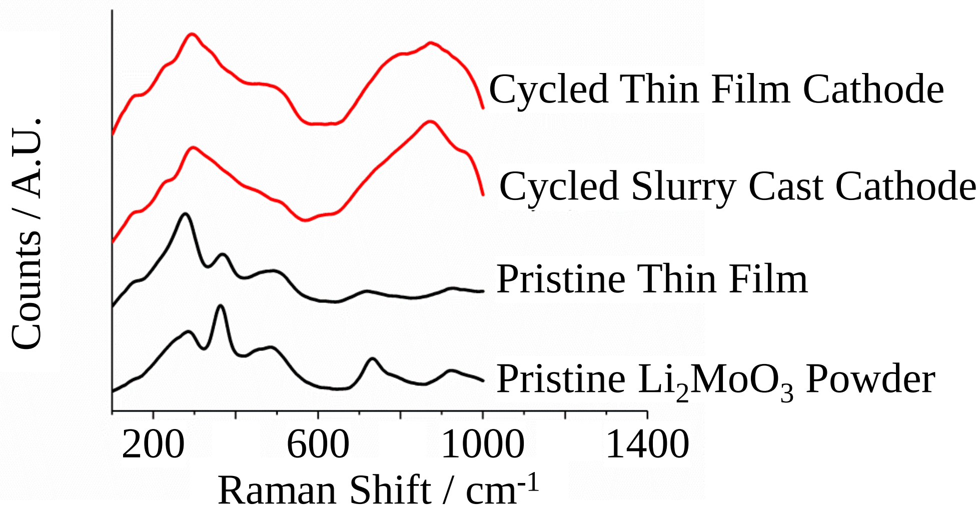
XRD



- Desired thin film structure confirmed via Raman and XRD
- Differences in Raman peak intensity attributed to preferential crystallographic orientation of thin film

With A.K. Kercher, ORNL

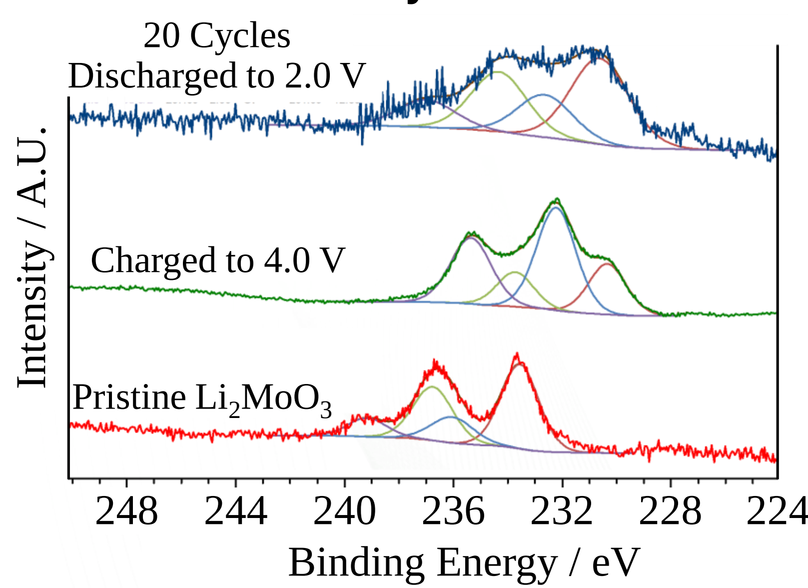
Ex-Situ Raman and XPS characterization of thin film Li_2MoO_3 cathodes provides additional insight on charge compensation mechanism



1. Band broadening indicates amorphization during cycling
2. Good agreement between thin film and slurry cast cathodes

1. Pristine Li_2MoO_3 contains significant amount of Mo^{6+}
   - Surface layer composed of Li_2MoO_4 (not detectable by XRD or Raman)
2. Cycled cells contain mixed oxidation states Mo^{4+}/Mo^{6+}
   - Result consistent with formation of disordered glassy phase

XPS Analysis: Mo3d



Sample	Mo^{4+} (at%)	Mo^{6+} (at%)
Pristine	0	100
Charged to 4.0V	32.0	68.0
Discharged to 2.0V	67.9	32.1

XPS analysis performed by N. Phillips

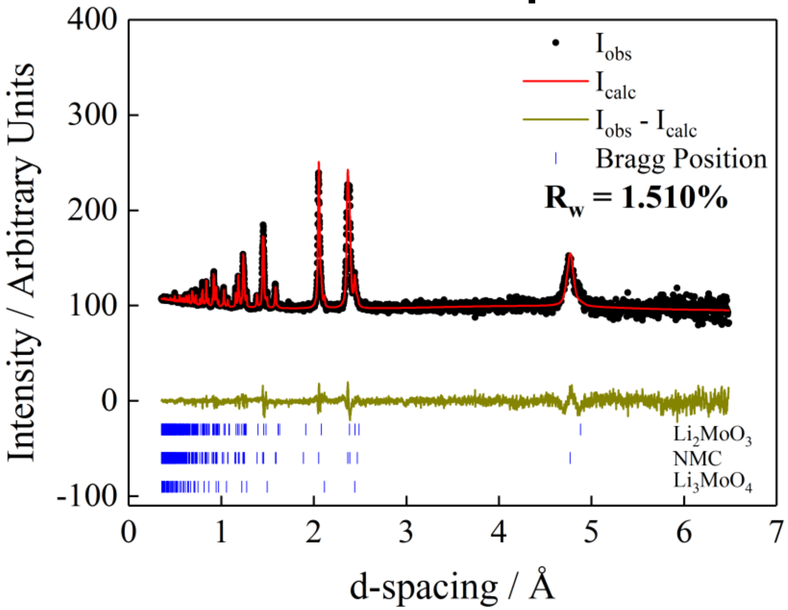
Self et al., Unpublished 2018

Composite cathodes with the formula $0.15Li_2MoO_3 \bullet 0.85LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ were synthesized, and their structure was analyzed using neutron and X-ray diffraction

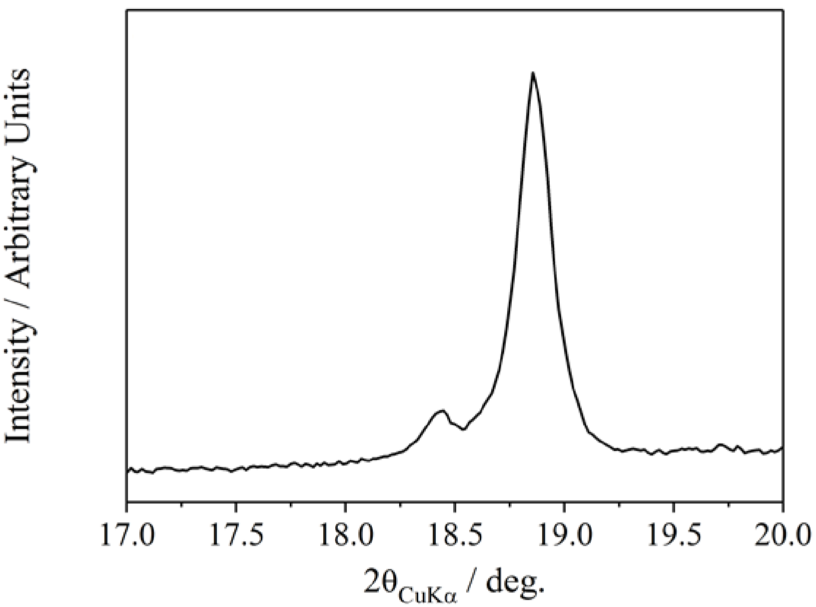
Synthesis Route

High energy ball milling to blend Li_2MoO_3 + NMC powders followed by firing (850°C)

Ball-Milled Composite



(003) Reflection Splitting



- NMC and Li_2MoO_3 have desired $R\bar{3}m$ symmetry
- Composite is two-phase mixture with minor Li_3MoO_4 impurity phase (~5%)

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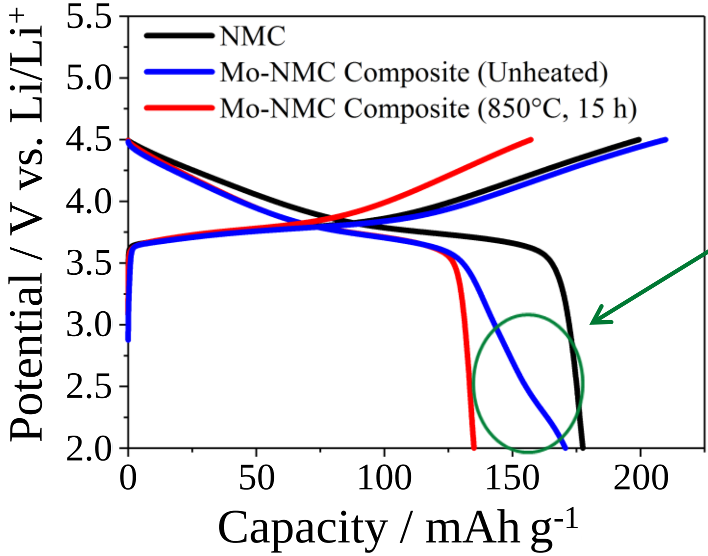
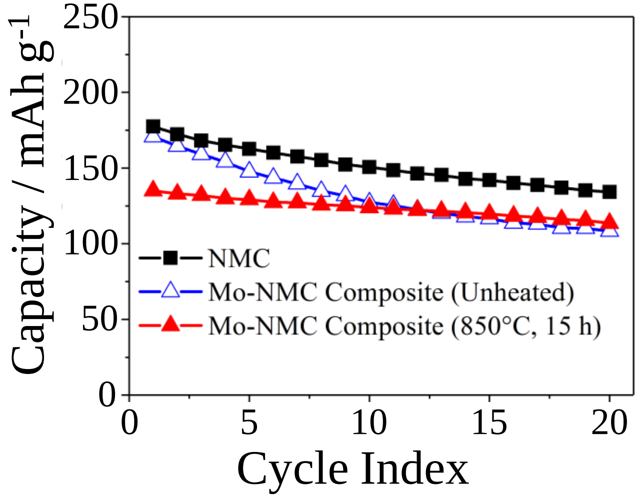
Electrochemical properties of Mo-NMC composite cathodes with and without heat treatment were compared with NMC

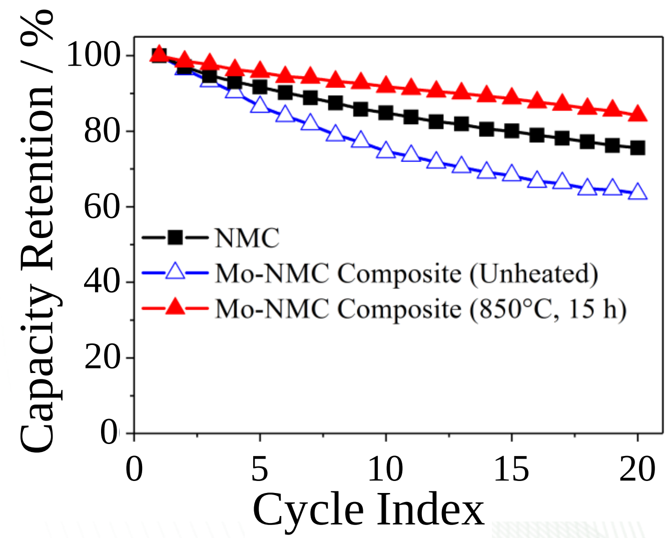


Unheated Composite:
- Discharge profile is superposition of endmembers

Heated Composite:
- $Ni^{3+/4+}$, $Mn^{3+/4+}$, and $Co^{3+/4+}$ are main redox centers



Capacity Normalization



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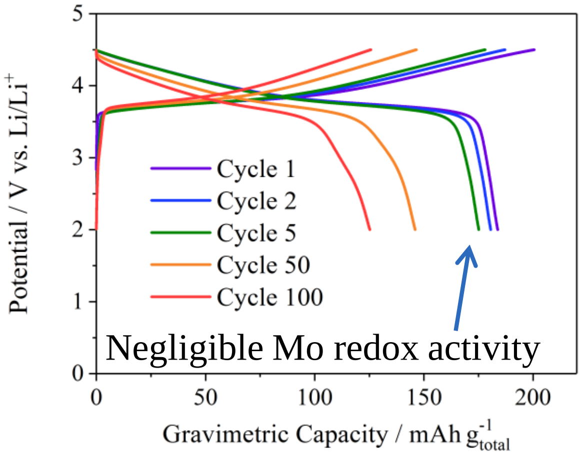
Substitution of Mo into NMC structure decreases electrochemical capacity but improves cycling stability.

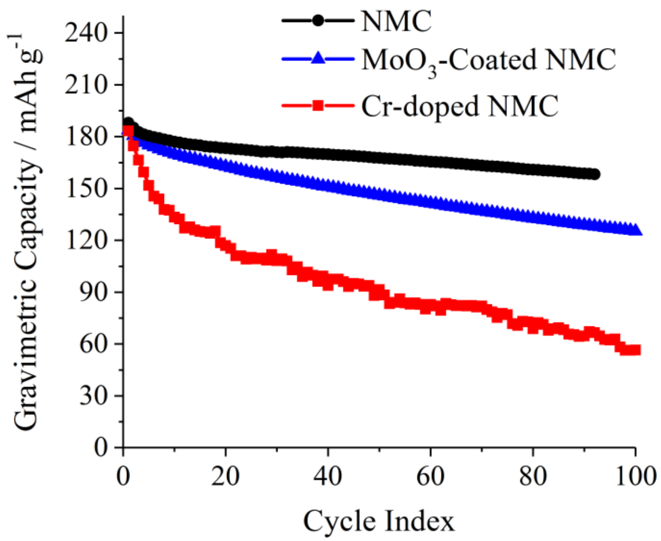
As an alternative to Cr substituted Li_2MoO_3 cathode (part of milestone-2) Cr-doped NMC and MoO_3-coated NMC cathodes were synthesized and characterized.

All materials were phase-pure with layered $R\bar{3}m$ structure (XRD data not shown)

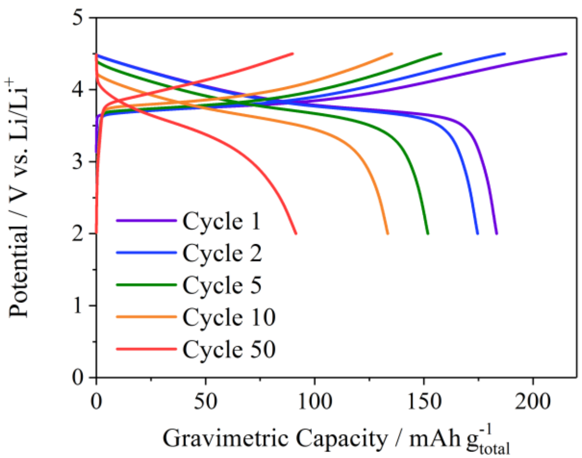
MoO_3-Coated NMC111



2.0-4.5V Cycling Performance vs. NMC



$LiNi_{0.317}Mn_{0.317}Co_{0.317}Cr_{0.05}O_2$



- MoO_3 coating and Cr-doping had no effect on the initial reversible capacity, but both materials showed accelerated capacity fade relative to baseline NMC
- Ni/Mn/Co $3^+/4^+$ are main redox centers in all materials
- Ongoing work is focused on optimizing doping and coating levels to improve cycling performance

Self et al., Unpublished 2018

Response to Reviewers Comments

Reviewer # 2 The cyclic stability of $Li_2Cu_xNi_{1-x}O_2$ has been marginally improved as shown in previous report, but the (low) voltage profile and low capacity are not attractive. Further, fairly good efforts were made in synthesizing and characterizing the molybdenum analogue of Li_2MnO_3 with greater oxygen stability through electrochemistry, XRD, and Raman. **Response :** We agree with reviewer's comment. $Li_2Cu_xNi_{1-x}O_2$ in our case was used as model system for demonstrating lattice oxygen loss at ~ 4V not mediated by any carbonate electrolytes. This effectively demonstrated the irreversible anion redox participation with substantial loss of electronegativity of oxygen.

Reviewer # 3 This project studied interesting oxide compounds of Li-rich Li_2MO_3 and Li_2MO_2. However, the reviewer could not see what merits these types of oxides have in developing high energy cathode materials. **Response :** We agree with reviewer's observation and in FY18 we have refocused our effort on Mo and Cr doping in NMC and molybdenum based composite cathodes as part of our strategy to stabilize oxygen loss at high voltage.

Reviewer # 4 Li_2MoO_3 may not be the right material due to its low capacity and conversion to amorphous state after the first cycle. **Response :** We clearly stated earlier that Li_2MoO_3 is studied in the context of using this as a structural unit for stabilizing the layered NMC cathode system. As part of FY 18 deliverable we have provided results on the first composite cathode system $x.Li_2MoO_3 \bullet (1-x)LiMO_2$

Oak Ridge National Laboratory

Collaborations and Coordination with other Institutions

Pacific Northwest NATIONAL LABORATORY

Electron Microscopy
Drs. Chongmin Wang & Pengfei Yan

BROOKHAVEN NATIONAL LABORATORY

In-operando X-ray Synchrotron Studies and Microscopy
Dr. Feng Wang

SLAC NATIONAL ACCELERATOR LABORATORY

Synchrotron X-ray microscopy and 3D microstructure
Dr. Johanna Nelson Weker

BERKELEY LAB Lawrence Berkeley National Laboratory

Modeling and oxygen activity of Li-excess compositions

Remaining Barriers and Challenges

- Determine if anionic substitution like fluorination can suppress oxygen evolution and enable high voltage operation.
- Investigate oxygen stability in Li-excess cation disordered cathodes.
- Determine the stability of cathode powders or electrodes in air, especially with respect to Li_2CO_3 formation on surface.
- Optimize the synthesis and electrochemical performance of cation disordered Li-excess compositions: Li_2MoO_3 and Li-excess Cr-substituted $LiMoO_2$.
- Develop approaches to mitigate lattice oxygen loss and improve structural stability of the cathode surface.

Any proposed future work is subject to change based on funding levels

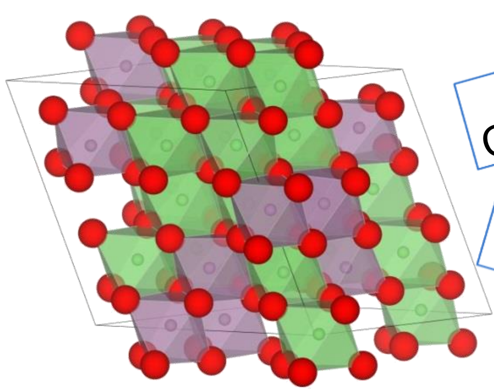
Proposed Future Research

1. We will continue our emphasis on synthesis and optimization of lithium-excess cation disordered oxides having rock salt and layered composition. Specific approaches include substitution of earlier TM elements such as Mo, Cr, and Ti. A few promising high capacity (and voltage) compositions include but are not limited to $Li_{1+x}Mo_yCr_{1-x-y}O_2$; $Li_{1+x}Nb_yMn_{1-x-y}O_2$; $Li_{1+x}Nb_yV_{1-x-y}O_2$; $Li_{1.2}Mn_{0.4}Ti_{0.4}O_2$.

2. As part of the cathode design and optimization process we will combine various spectroscopic, microscopic, and structural probes for the disordered cathode compositions to (i) understand the role of cation disorder/mixing for enhancing lithium diffusion pathways, (ii) contribution of oxygen redox participation and its reversibility and (iii) unique bonding and electronic structure that contributes to the extra capacity.

3. Undertake both anionic and cationic co-doping to stabilize the high capacity disordered cathodes. For example, simultaneous Mo or Nb and F substitution in $Li_{1+x}MO_2$ M = Mn, Ni

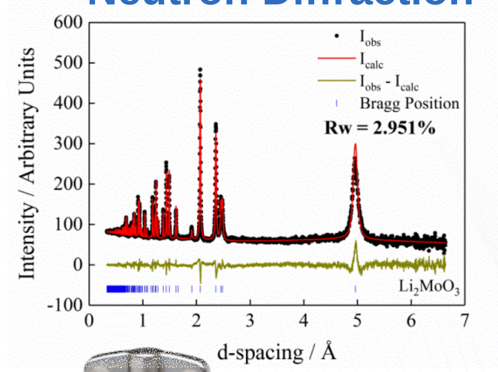
Disordered Li-Excess Cathode



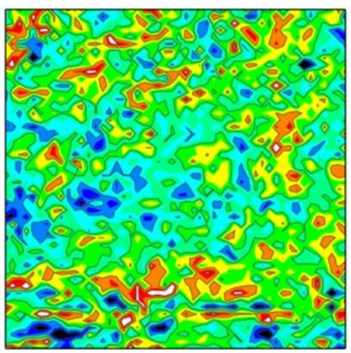
Structural Characterization

Oxygen Stability

Neutron Diffraction



Raman Mapping



Mass Spectrometry

OAK RIDGE National Laboratory

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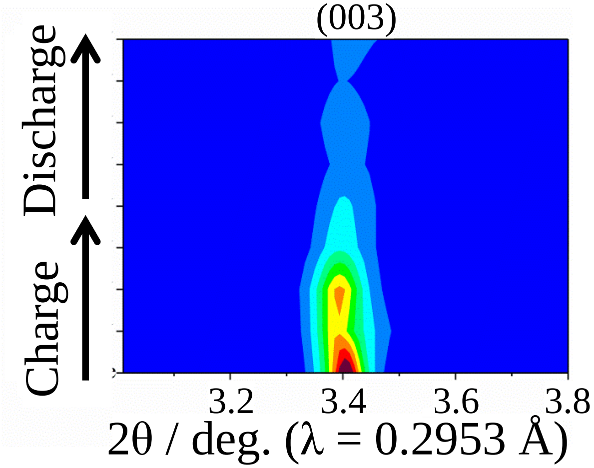
Summary

Technical Approach:

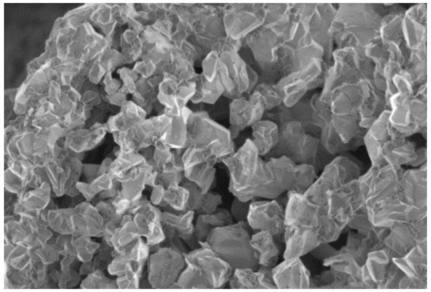
Synthesis and in-depth analysis of lithium-excess and multi-lithium chemistries for high voltage, high capacity cathodes

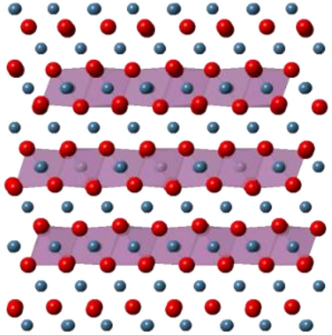
- Model driven synthetic approaches: solution-based, sol-gel and solid state methods.
- Diagnostic tools include a suite of microscopic, spectroscopic, and analytical techniques.
- Emphasis is placed on understanding and preventing oxygen loss at high voltage



Accomplishments:

- Identified chemical and structural changes that occur in Li_2MoO_3 cathodes during electrochemical cycling
- Unraveled mechanisms of electrochemical activity and degradation of Li_2MoO_3 cathodes using a combination of X-ray and neutron diffraction, Raman spectroscopy, electrochemistry, gas evolution experiments, and TEM.
- Developed synthesis routes to produce composite NMC-based cathodes containing a Li_2MoO_3 structural stabilizing unit





Ongoing work:

- Optimize the synthesis and processing of cation disordered Li-excess compositions.
- Investigate oxygen stability in disordered cathodes and continue to develop approaches to prevent oxygen loss.